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ANCIENT MARTIAN VALLEY GENESIS AND PALEOCLIMATIC INFERENCE: THE PRESENT AS A KEY TO THE PAST. G. R. Brakenridge, Surficial Processes Laboratory, Department of Geography, Dartmouth College, Hanover NH 03755, USA.

Understanding the origin of the relict fluvial landforms that dissect heavily cratered terrains on Mars is one of the clearest challenges to geomorphology to emerge in this century. The challenge is not being successfully met. Twenty years after the discovery of these landscapes we still do not know how the valleys formed or what they imply regarding paleoclimate. Geomorphology has not, to date, provided robust, remote-sensing-related analytical tools that are appropriate to the problem. It cannot because, despite the truism that "form follows function," landform genesis on Earth is not studied today by matching landform morphometries to genetic processes. Instead, the lithology, structure, and stratigraphy of the material underlying the landform is sought, and the local geological history may be investigated in order to understand the stage on which modern surficial processes are playing. Unfortunately, not much information other than morphometry has been assembled for the ancient martian valleys.

The problem is complicated by the relict nature of the landforms and the apparent need to infer genetic processes that are no longer occurring; the past must be reconstructed. To this end, geoscientists commonly use the principle of "uniformitarianism," wherein inferences regarding the past are based on the reality of the present. Consider the limitations that a comparative planetology approach presents, e.g., to a geologist from Mars attempting to understand the genesis of the now-relict Appalachian Mountains. Mars-Earth comparisons could not yield much insight. Understanding the passive margin Appalachians is critically dependent on a chain of insights regarding processes that derive from Earth's present. Terrestrial crustal plates move, and sea floor spreading, subduction, continental collision, and subsequent rifting occur. Inferring such processes would seem wildly speculative from a Mars perspective, and the genetic chain for creating relict mountains is indeed complex. However, we know that the Appalachians were in fact so created, and we gained such knowledge by extrapolation from the

present (e.g., the Himalayas). When investigating the genesis of relict fluvial valleys on Mars, we could do the same.

For example, immediately inside the rim of the 120-km-diameter crater Cerruli (located at ~+30°, 340°), 1-km-wide, flat-floored and (narrower) v-shaped valleys debouch from apparent 5–10-km-wide collapse depressions and extend for distances of a few tens of kilometers downslope and toward the center of the crater [1]. None of the valley landforms examined are cratered; they may have formed quite recently or may still be active. Intervening preserved highland remnants may be composed of ice-rich sedimentary material [1], and the large collapse depressions exhibit margin-proximal parallel lineations suggestive of margin-derived sediment input.

The terrain bears little resemblance to fluvial landscapes on Earth, but is similar to ancient, fluvially dissected terrain in Aëolis Quadrangle [2]. The flat-floored valleys do crudely resemble terrestrial glaciated valleys, and parabolic viscous drag-flow lineation is expressed locally on their smooth-surfaced floors, suggesting wall-to-wall longitudinal transport of debris and/or ice. However, these valleys exhibit scalloped margins and no snowfields feed their headwaters. Instead, and at varying distances upslope from the abrupt amphitheater headwalls, shallow closed depressions are visible in Viking Orbiter stereopairs (204S18-21), and these may indicate embryonic collapse and possible future headward growth of the valleys.

Viking-based stereoscopy also demonstrates that low-gradient or flat plains separate steep-gradient, incised, v-shaped valley reaches. At the limit of resolution, narrow channels on these plains appear to connect the valley reaches, but the incised reaches are perhaps more akin to avalanche chutes than to terrestrial fluvial valleys.

There is evidence for at least two different valley genesis pathways on sloping terrain inside Cerruli's complex crater rim: (1) collapse, linking of collapsed areas by growing flat-floored valleys, and transport of valley floor material in the downvalley direction even as valley widths grow, at least slightly, by mass-wasting; and (2) carving of much narrower, sometimes en echelon valleys along steep hillsides, coupled with suggestive evidence of intervening flow in channels on relatively flat terrain.

I offer here the speculative genetic hypothesis that the flat-floored landforms represent episodically active, sediment-laden valley glaciers formed by localized geothermal melting of abundant interstitial ice (permafrost) in a fine-grained sedimentary terrain. Geothermal melting may also localize spring heads for the narrow, deep, high-gradient valleys, or the collapse process itself may result in the generation of decanted, relatively sediment-poor overland water flows (some local evidence of fluid overtopping of the localized depressions exists). Whatever the genetic mechanisms for the suite of valley landforms, perhaps the most interesting observation is simply their youth. In aggregate, the morphologies are similar to the ancient valley systems cited as evidence for a previously much denser atmosphere on Mars.

If even very local valley genesis occurs today and the landforms are similar to those dating from ca. 3.8 Ga, then global climatic cooling may not be the most appropriate shut-off mechanism for the ancient valleys. Other mechanisms include (1) a change in planetary volcanism style from mainly effusive plains volcanism to plume eruptions [2], (2) changes in orbital parameters destabilizing ground ice at low latitudes but permitting stability at higher latitudes [3], or

(3) climatic warming, perhaps coeval to the termination of the Sun's T Tauri phase, and resulting poleward latitudinal shift of the zones of preserved ground ice.

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A CARBON DIOXIDE/METHANE GREENHOUSE ATMOSPHERE ON EARLY MARS. L. L. Brown and J. F. Kasting, Department of Geosciences, Pennsylvania State University, University Park PA 16802, USA.

One explanation for the formation of fluvial surface features on early Mars is that the global average surface temperature was maintained at or above the freezing point of water by the greenhouse warming of a dense CO₂ atmosphere [1]; however, Kasting [2] has shown that CO₂ alone is insufficient because the formation of CO₂ clouds reduces the magnitude of the greenhouse effect. It is possible that other gases, such as NH₃ and CH₄, were present in the early atmosphere of Mars and contributed to the greenhouse effect. Kasting et al. [4] investigated the effect of NH₃ in a CO₂ atmosphere and calculated that an NH₃ mixing ratio of $\sim 5 \times 10^{-4}$ by volume, combined with a CO₂ partial pressure of 4-5 bar, could generate a global average surface temperature of 273 K near 3.8 b.y. ago when the fluvial features are believed to have formed. Atmospheric NH₃ is photochemically converted to N₂ by ultraviolet radiation at wavelengths shortward of 230 nm; maintenance of sufficient NH₃ concentrations would therefore require a source of NH₃ to balance the photolytic destruction. We have used a one-dimensional photochemical model to estimate the magnitude of the NH₃ source required to maintain a given NH₃ concentration in a dense CO₂ atmosphere [5]. We calculate that an NH₃ mixing ratio of 10⁻⁴ requires a flux of NH₃ on the order of 10¹² molecules cm⁻² s⁻¹. This figure is several orders of magnitude greater than estimates of the NH₃ flux on early Mars; thus it appears that NH₃ mixed with CO₂ is not enough to keep early Mars warm.

We are currently using a one-dimensional radiative-convective climate model to determine the greenhouse effect of CH₄ in a CO₂ atmosphere. Atmospheric CH₄ would have a longer lifetime than NH₃ because CH₄ photolysis occurs only at wavelengths shortward of 145 nm, whereas NH₃ is photolyzed out to 230 nm. Hydrocarbon aerosols, which are formed as a product of CH₄ photolysis, are highly absorbent and may have provided a UV shield that would have lengthened the photochemical lifetime of CH₄ itself, as well as other hydrocarbon gases and NH₃. The greenhouse effect resulting from the combination of these gases and particles could conceivably have raised the mean global surface temperature of Mars to near the H₂O freezing point. A combination of radiative-convective climate modeling and photochemical modeling should show whether this idea is feasible and how large a CH₄ source would be needed.

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OXIDATION OF DISSOLVED IRON UNDER WARMER, WETTER CONDITIONS ON MARS: TRANSITIONS TO PRESENT-DAY ARID ENVIRONMENTS. R. G. Burns, Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge MA 02139, USA.

Introduction: The copious deposits of ferric-iron assemblages littering the surface of bright regions of Mars indicate that efficient oxidative weathering reactions have taken place during the evolution of the planet. Because the kinetics of atmosphere-surface (gas-solid) reactions are considerably slower than chemical weathering reactions involving an aqueous medium, most of the oxidation products now present in the martian regolith probably formed when groundwater flowed near the surface. This paper examines how chemical weathering reactions were affected by climatic variations when warm, wet environments became arid on Mars. Analogies are drawn with hydrogeochemical and weathering environments on the Australian continent where present-day oxidation of iron is occurring in acidic groundwater under arid conditions.

Background: Chemical weathering reactions of basaltic rocks are facilitated in aqueous solutions. Several stages are involved [1-3], including (1) dissolution of basaltic glass, iron sulfides, and ferromagnesian silicate minerals, which deliver soluble Mg²⁺, Fe²⁺, Ca²⁺, silica, etc., to groundwater; (2) ferrololysis, during which oxidation of dissolved Fe²⁺ occurs, producing soluble Fe³⁺ ions, which are eventually hydrolyzed to Fe(III) oxyhydroxy- and hydroxysulfate gels and colloids; and (3) precipitation of poorly crystalline ferric oxides, oxyhydroxides, and sulphate minerals, as well as clay silicate and evaporite minerals, in depositional environments such as the martian regolith.

Rates of chemical weathering of Fe²⁺-bearing minerals in aqueous environments that are applicable to the martian surface have been estimated from experimental data for basaltic minerals [2,3]. Reaction rates are strongly influenced by acidity or pH [4,5], as well as salinity or ionic strength [6], concentration of dissolved O in aerated groundwater [7,8], and temperature [7,8]. In acidic groundwater (pH < 4.5), silicate minerals dissolve rapidly, but rates of oxidation of aqueous Fe²⁺ ions are very slow, particularly in brines at low temperatures.

For example, rates of dissolution of olivine and pyroxenes range from about 1400 ppm Fe m⁻² yr⁻¹ (pH 2 at 25°C) to 2 × 10⁻² ppm Fe m⁻² yr⁻¹ (pH 6 at 0°C). In acidic ice-cold saline solutions (pH 4.5 at 0°C), dissolution rates are about 1 ppm Fe m⁻² yr⁻¹. In such melt waters saturated with O in the present-day martian atmosphere (P_{O₂} = 10⁻⁵ bar), the rate of oxidation of dissolved Fe²⁺ is also about 1 ppm Fe m⁻² yr⁻¹. Rates of oxidation are much higher in near-neutral pH saline groundwater and brines; thus, for brines with ionic strengths of 1 to 5 molal, rates of oxidation range from 500 to 900 ppm Fe m⁻² yr⁻¹ (pH 6 at 0°C) to about 100 ppm Fe m⁻² yr⁻¹ (pH 6 at -25°C). Such relatively low rates of oxidation of aqueous Fe²⁺ contrast with the very high values for terrestrial river water ($\approx 1.8 \times 10^7$ ppm Fe m⁻² yr⁻¹ for pH 6 at 25°C), and for deep ocean bottom water ($\approx 5 \times 10^6$ ppm Fe m⁻² yr⁻¹ for pH 8.2 at 2°C). On Mars, the rate of oxidation of dissolved Fe²⁺ in aerated near-neutral pH saline solutions would exceed the rate of supply of dissolved Fe, except in very acidic groundwater.

Calculations indicate that the mixing ratio of O in the present-day martian atmosphere is not being regulated by the oxidation of